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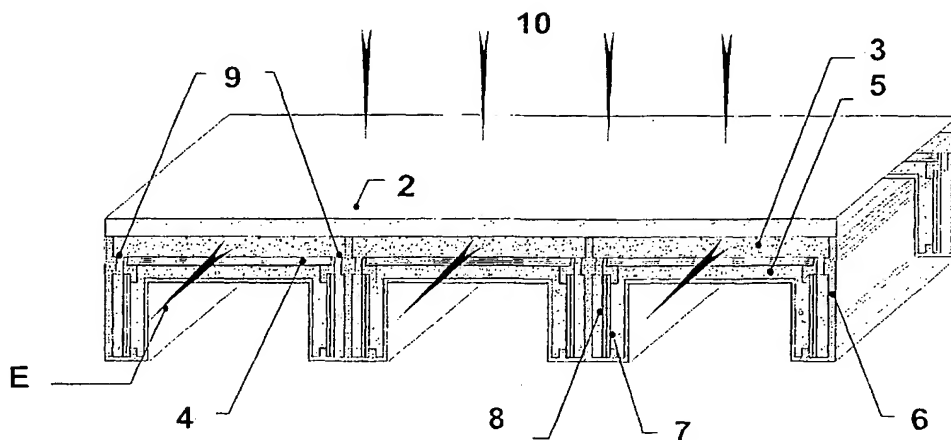
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(54) Title: INTEGRATED PHOTOELECTROCHEMICAL CELL AND SYSTEM HAVING A LIQUID ELECTROLYTE



(57) Abstract: An integrated photoelectrochemical (PEC) cell generates hydrogen and oxygen from water while being illuminated with radiation (10). The PEC cell employs a liquid electrolyte (2), a multi-junction photovoltaic electrode (4), and a thin ion-exchange membrane (7). A PEC system and a method of making such PEC cell and PEC system are also disclosed.

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## INTEGRATED PHOTOELECTROCHEMICAL CELL AND SYSTEM HAVING A LIQUID ELECTROLYTE

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### FIELD OF THE INVENTION

The instant invention relates generally to the generation of hydrogen and oxygen from water through a photo-electrolysis process and more particularly to the generation of hydrogen using solar radiation. This invention was made with Government support under National Renewable Energy Laboratory (NREL) contract No. NDJ-1-30630-08 awarded by the Department of Energy, and under ARL-WPAFB Grant "Photovoltaic Hydrogen for Portable, On-Demand Power" awarded to the University of Toledo under subcontract 03-S530-0011-01C1 under the primary contract F33615-02-D-2299 through the Universal Technology Corporation. The government has certain rights in this invention.

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### BACKGROUND OF THE INVENTION

Future transportation is widely believed to be based on a hydrogen economy. Using fuel cells, cars and trucks will no longer burn petroleum and will no longer emit CO<sub>2</sub> on the streets since they will use hydrogen as the fuel and the only byproduct is water. However, the reforming process, the main process that is used in today's hydrogen production, still uses petroleum-based products as the raw material and still emits large amounts of CO<sub>2</sub>. To reduce our society's reliance on petroleum based products and to avoid the emission of CO<sub>2</sub> that causes global warming, a renewable method of generating hydrogen must be developed. An electrolysis process using only sunlight and water is considered to be a top choice for hydrogen generation. Such hydrogen fuel is ideal for proton exchange membrane fuel cell (PEMFC) applications since it contains extremely low concentrations of carbon monoxide, which is poisonous to platinum catalysts in PEM fuel cells. However, indirect photo-electrolysis, in which the photovoltaic cells

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and electrodes are separated and connected electrically using external wires, is not cost-effective. An integrated photoelectrochemical cell (PEC) offers the potential to generate hydrogen renewably and cost effectively.

Several prior inventions and publications have disclosed designs for photoelectrochemical cells. U.S. Patent No. 4,090,933 (Nozik), U.S. Patent No. 4,144,147 (Jarrett et al.), U.S. Patent No. 4,236,984 (Grantham), U.S. Patent No. 4,544,470 (Hetrick), U.S. Patent No. 4,310,405 (Heller), U.S. Patent No. 4,628,013 (Figard et al.), U.S. Patent No. 4,650, 554 (Gordon), U.S. Patent No. 4,656,103 (Reichman et al.), U.S. Patent No. 5,019,227 (White et al.), U.S. Patent No. 6,471,850 (Shiepe et al.), U.S. Patent No. 6,361,660 (Goldstein), U.S. Patent No. 6,471,834 (Roe et al.).

J.R. Bolton "Solar photoproduction of hydrogen: a review", Solar Energy, 57, 37 (1996)

S.S. Kocha, D. Montgomery, M.W. Peterson, J.A. Turner, "Photoelectrochemical decomposition of water utilizing monolithic tandem cells", Solar Energy Materials & Solar Cells, 52, 389 (1998)

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P.K. Shukla, R.K. Karn, A.K. Singh, O.N. Srivastava, "Studies on PV assisted PEC solar cells for hydrogen production through photoelectrolysis of water", Int. J. of Hydrogen Energy, 27, 135 (2002)

X. Gao, S. Kocha, A. Frank, J.A. Turner, "Photoelectrochemical decomposition of water using modified monolithic tandem cells", In. J. of Hydrogen Energy, 24, 319 (1999)

R.E. Rocheleau and E.L. Miller, "Photoelectrochemical production of hydrogen: Engineering loss analysis", Int. J. Hydrogen Energy, 22, 771 (1997).

However, the prior art devices and methods described and disclosed in these above mentioned patents and publications have at least one of the following shortcomings:

the photovoltaic cell does not generate sufficient voltage to split water

the photovoltaic cell needs an external electrical bias for the electrolysis,

the photovoltaic device will not survive for extended use in the electrolyte due to inappropriate protection,

5 the photovoltaic device cannot be fabricated using low-cost methods, and

the photovoltaic device does not have potential for high conversion efficiency.

Therefore, there is a compelling and crucial need in the art for an  
10 efficient PEC device that produces hydrogen from water under radiation, does not require external bias due to sufficient voltage, and can be made at low cost.

### **SUMMARY OF THE INVENTION**

15 The instant invention provides a photoelectrochemical (PEC) cell that splits water under radiation and generates hydrogen and oxygen. In this PEC cell, a photovoltaic (PV) electrode, comprised of a multiple-junction solar cell and appropriate coatings and catalysts, is placed in an electrolyte, either acidic or alkaline. Under radiation such as sunlight, the PV electrode generates a  
20 voltage that is sufficient to drive electrolysis and produces hydrogen and oxygen. A membrane is installed in the PEC cell to allow exchange of ions for the electrolysis yet separate and confine the hydrogen and oxygen gases into two different compartments of the cell. A design that increases the efficiency of the hydrogen and oxygen production and minimizes the cost of the PEC cell  
25 is also disclosed.

The PV electrode uses a multiple-junction approach to generate a voltage sufficient to split water. The theoretical limit for water-splitting voltage is 1.23V. Practically, however, due to the existence of overpotentials at the electrolyte/electrode interfaces, the voltage needed is approximately 1.6V or  
30 greater. The PV structure that generates such a voltage under radiation, such

as sunlight, should have a voltage of approximately 1.6V or greater under operating conditions.

There are two ways to achieve the required voltage for water splitting in the multijunction electrode: 1) multi-junction photoelectrode in which all  
5 junctions are based on solid-state semiconductors and the top surface of the photoelectrode is covered with a layer of transparent, conducting and corrosion-resistant (TCCR) layer; and 2) multi-junction photoelectrode in which the top junction (the one facing on the side of radiation) is a liquid junction between a semiconductor layer and the electrolyte.

10 1) Multi-junction photoelectrode with all semiconductor junctions:

An example of this PV structure is a two-junction or three-junction amorphous silicon alloy solar cells stack which is comprised of semiconductor layers. The polarity of the photoelectrode can be in both ways, with either the  
15 the radiation, oxidation occurs on this side (anode) and oxygen gas is generated on the front surface (facing radiation) while hydrogen is generated in the back surface (on the substrate side, opposition to the radiation), which is the cathode.

In certain embodiments, transparent, conducting and corrosion-resistant coating is applied at the front surface of the photoelectrode to  
20 protect the semiconductor layers.

1A: Metal oxides as TCCR coatings

*Fluorine doped tin oxide*—Fluorine doped tin oxide ( $\text{SnO}_2\text{:F}$ ) is transparent, conducting and corrosion resistant. It can be deposited using  
25 many methods including sputtering, APCVD, etc.

*Titanium, tungsten and iron oxides*— $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{Fe}_2\text{O}_3$ , and modifications from these basic oxides, are stable in electrolyte. These oxides are alloyed with other elements to remove the rectifying junction between these oxides and electrodes. Various approaches including doping,  
30 alloying, and surface modification can be used to achieve an ohmic contact between these oxides and electrolyte.

### 1B: Nitrides and carbides as TCCR coatings

*Nitrides*—Various nitrides such as InGaN, GaPN, and GaAsPN are useful as the TCCR coating.

5 *Carbides*—Various carbide materials such as silicon carbide and germanium carbide are useful as the TCCR coating. Deposition technique such as very high frequency (VHF) plasma enhanced CVD and the hot-wire CVD are useful for these coatings.

### 1C: Polymer composites

10 Polymer nanocomposites can be made transparent and corrosion resistant. By adding a small amount of metal, these nanocomposite are made sufficiently conductive (needs to be  $<10^5 \Omega\cdot\text{cm}$ ) for use as the TCCR coating.

2) Hybrid multi-junction photoelectrode with semiconductor-electrolyte liquid junction as the top junction:

15 Wide gap compound semiconductor (WGCS) that forms an efficient junction with the electrolyte yet generates sufficient current so that it is matched with the other component solar cells in the multi-junction stack.

### 2A: Alloying of Metal Oxides to increase absorption

20 To increase the absorption and hence the photo generated electrical current,  $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{Fe}_2\text{O}_3$  are alloyed with other materials to have its bandgaps reduced. Useful candidate materials for the alloys include Ca and Mg.

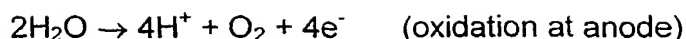
### 2B: III-V based compounds and carbides for liquid junction

25 III-V compound semiconductor materials such as n-type InGaN, GaPN, GaAsPN, and GaP and Group IV compound semiconductors such as SiC and GeC are useful for liquid junction with the electrolyte.

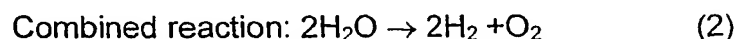
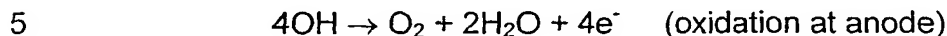
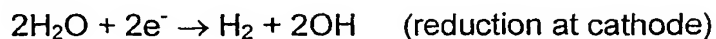
The electrolyte can be either acidic (such as  $\text{H}_2\text{SO}_4$ ) or alkaline (such as KOH). Examples of the half and combined reactions, for each type of the electrolyte is as following:

30 Acidic:





Or Alkaline:



The hydrogen and oxygen gases are produced in two different compartments, separated by a membrane. The membranes conduct ions but separate the gases. The membranes are installed in a way that allows for maximum radiation to reach the photoelectrode. In certain embodiments, one way for installing the membrane is to put the membrane in the same direction as the radiation. In another embodiment, another way is to put the membrane behind the substrate. A cation-exchange membrane is used for the conduction of  $\text{H}^+$  for the acidic electrolyte and anion-exchange membrane is used for the conduction of  $\text{OH}^-$  in the alkaline electrolyte. When the membranes are installed perpendicular to the photoelectrode (for example, vertically), the hydrogen and oxygen gases can be separated also by gravity, away from the membrane. In this way, the required thickness of membrane is small, leading to significant reduction in material cost and increased conduction of ions.

This instant invention also provides a PEC system that integrates the above-disclosed PEC cell with supporting structures and auxiliary components which form a stand-alone system for hydrogen generation. In such a system, electrolyte is circulating through the PEC system, flushing out gas bubbles and providing water for electrolysis. Such a PEC system is completely self-sustained. The supporting structure and auxiliary components include the mounting mechanisms of various components, mechanisms for electrolyte circulation through the PEC cell, and, when and where needed, containers to collect hydrogen and oxygen gases.

The instant invention further provides a method to fabricate the above disclosed PEC cell and PEC system.



The PEC cell described herein uses a small amount of electrolyte, making the system lightweight and portable. The PEC cell also increases the flow of electrolyte so that gas bubbles can be efficiently flushed out of, or removed from, the electrode surfaces. In certain embodiments, the PEC cell design uses a molded plastic contact and flat top pieces, making it easy to fabricate, thus reducing manufacturing costs.

The above disclosed PEC cell and system offer significant advantages such as high conversion efficiency, efficient electrolysis, low cost, and high durability. It is understood that, in certain embodiments, for PEM fuel cells (PEMFC) where Pt is used as a catalyst, Pt could be poisoned by CO gas, thus resulting in reduced performance. However, the hydrogen fuels generated using such a PEC system contain extremely low amount of carbon monoxide, making such hydrogen ideal for PEMFC. The above-mentioned PEC system, when used in combination with portable fuel cells, provides distributed, and portable, power generation. The energy can be stored in hydrogen form. Since there is radiation such as sunlight everyday, the required storage for such combined PEC/PEMFC system does not need to be large, thus resulting in reduced costs.

The foregoing has outlined in broad terms the more important features of the invention disclosed herein so that the detailed description that follows may be more clearly understood, and so that the contribution of the instant inventor to the art may be better appreciated. The instant invention is not to be limited in its appreciation to the details of the construction and to the arrangements of the components set forth in the following description or illustrated in the drawings. Rather, the invention is capable of other embodiments and of being practiced and carried out in various other ways not specifically enumerated herein. Finally, it should be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting, unless the specification specifically so limits the invention.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figs. 1a, 1b and 1c are schematic diagrams of the PEC cell showing the PV electrode, the membrane, and the two compartments separated by the membrane. Fig. 1a is the front sectional view while Fig. 1b is the top view. Fig. 1c is a three-dimensional schematic diagram showing more details of the PEC system.

Fig. 2 is a front view of selected amorphous silicon based double-junction solar cell, as an example of the PV structure.

Fig. 3 is a schematic of the end adaptor of the PE cell for the collection of hydrogen and oxygen gases and circulation of electrolyte. Fig. 3a is a front view and Fig. 3b is the top view.

Fig. 4 is a schematic diagram of the side view of the PEC cell with end adaptors.

Fig. 5 is a schematic diagram of the PEC system, showing the electrolyte circulation mechanism and gas containers.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In one aspect, the present invention relates to a photoelectrochemical (PEC) cell having at least one photovoltaic electrode that generates voltage under radiation; at least one electrolyte; a container that confines electrolyte; a top cover that is substantially transparent to radiation; at least one mechanism that separates the container into two compartment for oxidation and reduction reactions; and a structure that allows maximum radiation to reach the active area of the photoelectrode. In certain aspects, the PEC cell has a top-most junction that is closest to the radiation in the photovoltaic electrode and the top-most junction comprises a liquid junction between a semiconductor and the electrolyte. In other aspects, the semiconductor that forms a junction with the electrolyte comprises at least one metal oxide that is stable in the electrolyte.

### Description of the PEC cell

An example of the PEC cell is depicted in Fig. 1a. The PEC cell 1 consists of a top cover 2, a holder/container 6, a photovoltaic electrode 4, membranes 7 and other components. The photoelectrode 4 and membrane 7 separate the PEC cell into two compartments 3 and 5, in which oxidation and reduction half reactions take place, respectively. The photoelectrode 4, under radiation 10, which penetrates through the largely transparent top cover 2, generates a voltage that is around or above 1.6 eV and is sufficient to drive water electrolysis. The photoelectrode 4 is a photovoltaic cell comprised of a stack, or plurality of, layers of semiconductor materials, deposited on a conducting substrate, as will be described in detail below.. The two sides of the photoelectrode serve as the anode and cathode, respectively. The polarity depends on the sequence of the p-type and n-type doped layers in the semiconductor stack, which forms the photovoltaic cell 4. A thin coating of membrane 7 applied on a support 8 allows the exchange of ions while separating gases generated in the anode and cathode inside the two compartment 3 and 5, respectively.

When radiation 10 such as sunlight is irradiated on the photoelectrode 4 through the largely transparent top cover 2, a voltage is generated. When a multiple-junction photovoltaic cell is used, the voltage can be around or higher than 1.6 V, which is sufficient for water electrolysis. Hydrogen and oxygen are generated in the two compartments. If the p-type semiconductor layer is at a top side 4-1 of the electrode 4 in Fig. 1, i.e., facing radiation 10 and closer to compartment 3, and n-type semiconductor layer is at a bottom side 4-2 of the electrode 4, a positive electrical bias is then generated at the top surface 4-1, the anode, and a negative bias is generated at the bottom surface 4-2, the cathode. Oxygen is recovered from of the top compartment 3 and hydrogen is recovered from the bottom compartment 5. If the polarity of the semiconductor layers comprising the

electrode 4 is reversed, the reduction and oxidation reactions will switch sides.

Both acidic and basic electrolytes are useful for the electrolysis. An example of the acidic electrolyte is  $\text{H}_2\text{SO}_4$  and an example of alkaline electrolyte is KOH. The membrane 7 is applied onto a porous substrate 8. the porous substrate 8 allows electrolyte to flow through the substrate 8 yet provides mechanical strength to support the membrane 7. The membrane 7 can be made to be extremely thin to reduce cost. An example of the supporting material is micro-porous polypropylene.

The PEC cell 1 further includes via holes 9 which are defined by at least one mounting mechanism 9-1. The via holes 9 allow the electrolyte E flow through the membrane 7. In certain embodiments, the holder/container 6 can be made of plastic, glass or other suitable materials that provide mechanical support yet are resistant to the corrosion from the electrolyte. Also, in certain embodiments, there can be flow guides 3-1 and/or 5-1 are installed in the compartments 3 and 5, causing the sideways flow of electrolyte in a zig-zag form. The flow guides 3-1 and/or 5-1 can increase the conduction of ions and promote rapid electrolysis.

In an alternative embodiment, rather than having a membrane in the PEC cell, the PEC cell is designed such that the PEC cell makes the best use of gravity to separate the gases generated in different compartments. In this way, the use of membrane can be minimized or totally avoided.

Fig. 1b is a top view of the PEC cell 1 shown in Fig. 1a, showing the via holes 9 and the photoelectrode 4. The electrolyte, in the separate compartments 3 and 5 flows in the direction parallel to the photoelectrode (upward in Fig. 1b). FIG. 1c is a three-dimensional view of the PEC cell showing some of the details depicted in FIG. 1a and FIG. 1b.

Fig. 2 shows an example of the photoelectrode 4. Amorphous silicon (a-Si) and a-Si based alloys are used as the semiconductor layers in this example. The structure of the photoelectrode shown in Fig. 2 is: metal substrate 21, metal reflector 20, transparent conducting oxide (TCO) 19, n-

type a-Si layer 18, intrinsic a-SiGe layer 17, p-type a-Si based layer 16, n-type a-Si layer 15, intrinsic a-Si layer 14, p-type a-Si based layer 13 (nipin layers), TCO layer 12. The substrate 21 is coated with a hydrogen evolution catalyst 22 and the top TCO layer 12 can be covered with oxygen evolution catalyst 11. Examples of the top TCO layers 12 are tin oxide and fluorine-doped tin oxide. The nipin layers create a positive voltage bias on the top under sunlight such that oxygen evolves into the top compartment 3 and hydrogen evolves into the lower compartment 5.

An alternative structure is: metal substrate 21, metal reflector 20, transparent conducting oxide (TCO) layer 19, p-type a-Si based layer 18, intrinsic a-SiGe layer 17, n-type a-Si layer 16, p-type a-Si based layer 15, intrinsic a-Si layer 14, n-type a-Si layer 13 (pinpin layers), TCO layer 12. The substrate 21 is coated with a oxygen evolution catalyst 22 and the top TCO layer can be covered with hydrogen evolution catalyst 11. The pinpin layers create a negative voltage bias on the top layer 12 under sunlight such that hydrogen evolves into the top compartment 3 and oxygen evolves into the lower compartment 5.

Fig. 3 shows an end adaptor 23 that delivers electrolyte to the PEC cell 1 or collects electrolyte mixed with oxygen or hydrogen bubbles from PEC cell 1. A top, or first, opening 24 is operatively connected to the top compartment 3 while a bottom, or second, opening 25 is operatively connected to the bottom compartment 5. In the adaptor 23 shown in Fig. 3, electrolyte flows out of PEC cell 1 into first and second openings 24 and 25, then into first and second channels 26 and 27 which are operatively connected thereto, and out of first and second outlet tubes 28 and 29, respectively. Fig. 3a is the front sectional view while Fig. 3b is the top view of the end adaptor 23. Fig. 4 shows a side view of a PEC cell with first and second end adaptors 23 and 23' connected to the PEC cell 1 to allow electrolyte to flow out of and into the PEC cell, respectively.

### Description of the PEC system

Fig. 5 shows a PEC system 50 that uses the PEC cell 1 to generate hydrogen and oxygen. This figure shows the side view as in Fig. 4. In one example, the photoelectrode is an nipnip type cell with positive voltage generated on the radiation side. Hydrogen gas is generated in compartment 5 and exits from the first outlet tube 28 at the end adaptor 23. Oxygen is generated in compartment 3 and exits from the second outlet tube 29. In the embodiment shown, first and second pumps 31 and 39 are used for electrolyte circulation. The gases and electrolyte are circulated by the pumps 31 and 39 into first and second gas collection containers 34 and 42, respectively, through first and second gas collection inlets 36 and 44, respectively. The hydrogen gas is collected at a first collection port 38 on the first gas collection container 34 and the oxygen gas is collected at a second collection port 46 on the second gas collection container 42. Electrolyte flows out of the first and second gas collection containers 34 and 42 through at first and second recycling ports 37 and 45, respectively, back into the compartments 5 and 3 through inlet tubes 28' and 29' in the second end adaptor 23'. When the electrolyte levels 35 and 43 in the first and second gas collection containers 34 and 42, respectively, are low, the respective water inlet valves and switches 32 and 40 will open, allowing additional water to flow into the system via first and second water inlet ports 33 and 41, respectively.

### Method to make the PEC cell and PEC system

It is to be understood that the present invention contemplates the use of several variations of methods to make the PEC cell 1 and PEC system 50. One example is described herein using the structure described in Figs. 1-5. A metal foil or plate 21 is used as the substrate. Catalyst 22 is deposited on the substrate (catalyst 22 can also be deposited after the TCO layer 12 is deposited). A reflective metal layer 20, such as aluminum layer, and a TCO layer 19, such as tin oxide or zinc oxide, are then deposited on

the metal substrate 21 via thin film deposition processes such as evaporation, sputtering or other suitable methods. This is then followed by deposition of semiconductor layers, such as a-Si based semiconductor layers 13-18. Another TCO layer 12 is then deposited on the topmost layer of the electrode 4. In certain embodiments a thin layer of catalyst can be applied on a top surface of the TCO layer 12. An example of such catalyst is a thin layer of carbon powder with micrometer sized spheres that support nanometer sized Pt particles. The carbon powder can be pressed or bonded to the TCO layer 12. The catalyst on the front surface can be applied to selected regions so that it does not block, or does not block as much of, the incoming radiation, such as sunlight.

In fabrication of the membranes, thin coatings of membrane, such as Nafion<sup>®</sup>, a product of Dupont is a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups, can be applied onto an inexpensive support 8, such as micro-porous polypropylene. The membrane 7 can be made to have a desired thinness to reduce cost.

It is to be understood that the present invention can be sealed or contained in a suitable holder/container 6. The holder/container can be made of plastic, glass, metal or other materials. The selection of the holder/container material depends on the cost, mechanical strength, and corrosion resistance. The holder/container, such as plastic, can be made using a molding process. The via holes 9 and various mounting mechanisms 9-1 for the photoelectrode and the membrane can be molded on the plastic support/container. After the photoelectrodes 4 are installed inside the container 6, the edges 4-3 and/or 4-4 of the photoelectrode 4 can be protected with a suitable insulating material 9-2, such as an epoxy material.

The container 6 is sealed with the top cover 2, which can be made out of glass, plastic or other materials largely transparent to the radiation.

The end adapter pieces 23 and 23', described in Fig. 3, can be machined to fit the PEC cell 1. Two end adapters, with gas tubes 28, 29, 28'

and 29', are installed to the PEC cell for electrolyte inlet and water/gas outlet. Circulation pumps, water inlet valves, and the gas collection containers are installed using gas tubes. Hydrogen and oxygen are collected at port 38 and port 46, respectively, or vice versa, depending on the polarity of the photovoltaic structure.

#### Method to make hydrogen and oxygen

The PEC system 50, with an example shown in Fig. 5, is used to generate hydrogen and oxygen. The system is installed under radiation of sunlight or other suitable radiation such that the radiation enters through the top cover 2. Water is added in ports 41 and 33; hydrogen and oxygen gases are collected at ports 38 and 46, respectively. In using the PEC system, the PEC cell is preferably tilted so that the top cover 2 faces the radiation such as the sunlight. Electrolyte is fed into the lower end-adaptor 23' and removed from the higher end-adaptor 23. In this way, gravity drives gas bubbles out of the PEC cell and circulates the electrolyte.

#### Examples

The photoelectrode can be made using different types of solar cells. Both two-junction and three-junction a-Si based solar cells can be used, for example.

When a two-junction a-Si/a-SiGe solar cell is used, the total voltage can be made to be around 1.6V or higher at operating point, when relative low Ge content is used for the absorber layers. In one embodiment, a specific structure comprises:

stainless steel/aluminum/ZnO/a-Si n/ a-SiGe intrinsic/a-Si p or nanocrystalline p/ a-Si n/a-Si intrinsic/a-Si p or nanocrystalline p/SnO<sub>2</sub>:F.

The thickness of the respective layers, are approximately: 0.1mm/100nm/500nm/10nm/150nm/10nm/10nm/150nm/10nm/200nm, respectively, for optimum sunlight radiation.



The width of each sections of photoelectrode 4 is around 5 to 10 cm while the length can be in the order of 1 m. The optimum width of electrode is determined by the effective ion conduction, the largest active area of electrode under the sunlight, and lowest materials and fabrication costs.

5        In certain embodiments, the thickness and bandgap of a-Si and a-SiGe intrinsic layers are adjusted such that the two component solar cells generate about the same electrical current under the radiation specified. For electron radiation, it is desired that the thickness of the i-layers be much thicker than for photon radiation.

10        In certain embodiments, the photovoltaic electrode comprises at least one of the following solar cell types: amorphous silicon (a-Si), cadmium telluride (CdTe), copper indium diselenide (CuInSe<sub>2</sub>), copper indium gallium diselenide (CIGS), III-V (GaAs, InP etc), crystalline silicon (c-Si), thin film silicon (thin-Si), or variations and combinations thereof. Further, in certain  
15        embodiments, the photovoltaic electrode has multiple junctions including two-junctions, three junctions and more junctions wherein sufficient voltage is generated for electrolysis. In still other embodiments, at least one of the photovoltaic junctions in the multiple-junction photoelectrode uses amorphous silicon.

20        In other embodiments, triple-junction a-Si/a-SiGe/a-SiGe, a-Si/a-Si/a-SiGe, a-Si/a-SiGe / $\mu$ c-Si, or a-Si/ $\mu$ c-Si/ $\mu$ c-Si solar cells is also used to generate sufficient voltage instead of using a tandem solar cells with two junctions. Further, in certain embodiments, a top-most junction is closest to the radiation in the photovoltaic electrode and comprises a solid-state  
25        junction generated between p-type and n-type semiconductors.

      The above detailed description of the present invention is given for explanatory purposes. All references disclosed herein are expressly incorporated herein by reference. It will be apparent to those skilled in the art that numerous changes and modifications can be made without departing  
30        from the scope of the invention. Accordingly, the whole of the foregoing

description is to be construed in an illustrative and not a limitative sense, the scope of the invention being defined solely by the appended claims.

CLAIMS

We claim:

1. A photoelectrochemical (PEC) cell, comprising:  
at least one photovoltaic electrode that generates voltage under  
5 radiation;  
at least one electrolyte;  
a container that confines electrolyte;  
a top cover that is substantially transparent to radiation;  
at least one mechanism that separates the container into two  
10 compartment for oxidation and reduction reactions; and  
a structure that allows sufficient radiation to reach the active  
area of the photoelectrode.
2. The PEC cell as in claim 1, wherein the photovoltaic electrode  
15 comprises at least one of the following solar cell types: amorphous silicon  
(a-Si), cadmium telluride (CdTe), copper indium diselenide (CuInSe<sub>2</sub>),  
copper indium gallium diselenide (CIGS), III-V (GaAs, InP etc), crystalline  
silicon (c-Si), thin film silicon (thin-Si), or variations and combinations  
thereof.
- 20 3. The PEC cell as in claim 2, wherein the photovoltaic electrode  
has multiple junctions including two-junctions, three junctions and more  
junctions wherein sufficient voltage is generated for electrolysis.
- 25 4. The PEC cell as in claim 3, wherein at least one of the  
photovoltaic junctions in the multiple-junction photoelectrode uses  
amorphous silicon.
5. The PEC cell as in claim 3, wherein a top-most junction is  
30 closest to the radiation in the photovoltaic electrode and the top-most

junction comprises a liquid junction between a semiconductor and the electrolyte.

5        6.        The PEC cell as in claim 5, wherein the semiconductor that forms a junction with the electrolyte comprises at least one metal oxide that is stable in the electrolyte.

10        7.        The PEC cell as in claim 6, wherein the metal oxide comprises  $\text{TiO}_2$ ,  $\text{WO}_3$  or  $\text{Fe}_2\text{O}_3$  and combinations thereof.

      8.        The PEC cell as in claim 6, wherein the metal oxide is alloyed with at least one another material, including Ca and/or Mg, to increase radiation absorption.

15        9.        The PEC cell as in claim 5, wherein the semiconductor that forms a junction with the electrolyte comprises at least one III-V compound semiconductor that is stable in electrolyte.

20        10.       The PEC cell as in claim 9, wherein the III-V compound semiconductor includes at least one of: InGaN, GaPN, GaAsPN, GaP and combinations thereof.

25        11.       The PEC cell as in claim 5, wherein the semiconductor that forms a junction with the electrolyte comprises at least one Group IV semiconductor or semiconductor alloy that is stable in electrolyte.

      12.       The PEC cell as in claim 11, wherein the Group IV semiconductor or semiconductor alloy includes at least one of: Si, C, Ge, Sn, SiC, GeC and combinations thereof.

13. The PEC cell as in claim 3 wherein a top-most junction is closest to the radiation in the photovoltaic electrode and comprises a solid-state junction generated between p-type and n-type semiconductors.

5        14. The PEC cell as in claim 13, wherein the photoelectrode is coated with a layer of transparent, conducting and corrosion-resistant (TCCR) layer.

10        15. The PEC cell as in claim 14, wherein the TCCR layer comprises a metal oxide based material.

16. The PEC cell as in claim 15, wherein the metal oxide TCCR layer comprises  $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{Fe}_2\text{O}_3$ , and combination thereof.

15        17. The PEC cell as in claim 15, wherein the metal oxide TCCR layer is doped with at least one other element, including F, Cl and mixtures thereof, to increase resistance to corrosion.

20        18. The PEC cell as in claim 15, where in the metal oxide TCCR layer is doped with at least one other element to reduce or remove a rectifying junction between the oxide and the electrolyte and to reduce junction resistance.

25        19. The PEC cell as in claim 14, wherein the TCCR layer comprises a nitride compound.

30        20. The PEC cell as in claim 19, wherein the nitride compound comprises InGaN, GaPN, GaAsPN or variations and combinations of thereof, including both crystalline and amorphous forms.

21. The PEC cell as in claim 14, wherein the TCCR layer comprises a carbide compound.

22. The PEC cell as in claim 21, wherein the carbide compound comprises SiC, GeC, or variations and combinations of thereof, including both crystalline and amorphous forms.

23. The PEC cell as in claim 14, wherein the TCCR layer comprises a polymer based composite.

10

24. The PEC cell as in claim 23, wherein the TCCR polymer based composite comprises nanocomposite materials with a fraction of metal embedded inside to increase electrical conductivity.

25. The PEC cell as in claim 3, wherein the radiation comprises photons, electrons or other energy-carrying radiations and particles.

26. The PEC cell as in claim 25, wherein the radiation comprises solar radiation.

20

27. The PEC cell as in claim 3, wherein the mechanism that separates the container into two compartments comprises at least one thin ion-exchange membrane.

28. The PEC cell as in claim 27, wherein the membrane comprises at least one of a cation exchange membrane or an anion-exchange membrane.

29. The PEC cell as in claim 27, wherein the ion-exchange membrane is installed perpendicular to the photoelectrode to allow for maximum radiation to reach the photoelectrode.

30

30. The PEC cell as in claims 27, wherein the ion-exchange membrane is installed behind the photoelectrode and away from the radiation to allow for maximum radiation to reach the photoelectrode.

5

31. The PEC cell as in claim 30, wherein the membrane comprises a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups

10 32. The PEC cell as in claim 31 wherein the membrane is applied onto a support.

33. The PEC cell as in claim 32 wherein the support comprises micro-porous polypropylene.

15

34. The PEC cell as in claim 3, wherein the electrolyte is acidic.

35. The PEC cell as in claim 3, wherein the electrolyte is alkaline.

20 36. The PEC system comprising the PEC cell as in claim 3 and further comprising at least one collecting mechanism to collect gases generated by the PEC cell.

25 37. The PEC system as in claim 36 comprising at least one end adaptor that delivers electrolyte to the PEC cell.

38. The PEC system as in claim 36 comprising collecting electrolyte mixed with oxygen or hydrogen bubbles from the PEC cell.

30 39. The PEC system as in claim 37, wherein the end adaptor comprises a top opening operatively connected to a top compartment and a

bottom compartment opening operatively connected to a bottom compartment, wherein electrolyte flows out of the PEC cell into both the top opening and the bottom opening, through a first channel and a second channel operatively connected to the top and bottom openings, respectively, and out of first and second outlet tubes operatively connected to the first and second outlet tubes, respectively.

40. The PEC system as in claim 39, wherein the photoelectrode is an nipnip type cell with positive voltage generated on a radiation side.

41. The PEC system as in claim 39, wherein the photoelectrode is an pinpin type cell with negative voltage generated on a radiation side.

42. The PEC system as in claim 40, wherein hydrogen gas is generated in the bottom compartment and exits from the first outlet tube, and wherein oxygen is generated in the top compartment and exits from the second outlet tube.

43. The PEC system as in claim 41, wherein oxygen gas is generated in the bottom compartment and exits from the first outlet tube, and wherein hydrogen is generated in the top compartment and exits from the second outlet tube.

44. The PEC system as in claim 42, further comprising first and second pumps for circulating electrolyte wherein gases and electrolyte are circulated by the pumps through first and second gas collection containers, respectively, so that hydrogen is collected at a first collection port in a first gas collection container and oxygen is collected at a second collection port in a second gas collection container; and wherein electrolyte flows from the first and second recycling ports, respectively, back into the bottom and top



compartments respectively, through third and fourth inlet tubes operatively connected to a second end adaptor on and opposing end of the PEC cell.

45. The PEC system as in claim 43, further comprising first and  
5 second pumps for circulating electrolyte wherein gases and electrolyte are circulated by the pumps through first and second gas collection containers, respectively, so that oxygen is collected at a first collection port in a first gas collection container and hydrogen is collected at a second collection port in a second gas collection container; and wherein electrolyte flows from the  
10 first and second recycling ports, respectively, back into the bottom and top compartments respectively, through third and fourth inlet tubes operatively connected to a second end adaptor on and opposing end of the PEC cell.

46. The PEC system as in claim 44, further comprising first and  
15 second water inlet valves and switches operatively connected via first and second ports, respectively, to the first and second gas collection containers to allow additional water to flow into the system.

47. The PEC system as in claim 45, further comprising first and  
20 second water inlet valves and switches operatively connected via first and second ports, respectively, to the first and second gas collection containers to allow additional water to flow into the system.

48. A method of making the PEC cell described in claim 3,  
25 comprising:

depositing a catalyst on a substrate,  
depositing a reflective metal layer and a first transparent conducting  
oxide (TCO) layer on the metal substrate via at least one suitable thin film  
deposition process,  
30 depositing a plurality of semiconductor layers on the TCO layer, and

depositing at least a second TCO layer deposited on a topmost layer of the semiconductor layers.

49. The method of making the PEC cell described in claim 48,  
5 wherein the substrate comprises a metal foil or plate.

50. The method of making the PEC cell described in claim 48,  
wherein the reflective metal layer comprises an aluminum layer.

10 51. The method of making the PEC cell described in claim 48,  
wherein the first transparent conducting oxide (TCO) layer comprises at  
least one of tin oxide or zinc oxide.

52. The method of making the PEC cell described in claim 48,  
15 wherein the thin film deposition process including at least one of  
evaporation, sputtering or other suitable deposition method.

53. The method of making the PEC cell described in claim 48,  
wherein the plurality of semiconductor layers comprises a-Si based  
20 semiconductor layers.

54. The method of making the PEC cell described in claim 48,  
wherein a thin layer of catalyst is deposited on the second TCO layer.

25 55. The method of making the PEC cell described in claim 48,  
wherein the catalyst comprises a thin layer of carbon powder with  
micrometer sized spheres that support nanometer sized Pt particles.

56. The method of making the PEC cell described in claim 48,  
30 wherein the carbon powder is pressed or bonded to the TCO layer.

57. The method of making the PEC cell described in claim 48, wherein the catalyst is applied to selected regions so that the catalyst does not substantially block incoming radiation.

5 58. The method of making the PEC system described in claim 32, comprising operatively connecting an end adaptor comprises a top opening to a top compartment and a bottom opening to a bottom compartment, wherein electrolyte flows out of the PEC cell into both the top opening and the bottom opening, through a first channel and a second channel  
10 operatively connected to the top and bottom openings, respectively, and out of first and second outlet tubes operatively connected to the first and second outlet tubes, respectively.

59. The method as in claim 58 wherein the photoelectrode is an  
15 nipnip type cell with positive voltage generated on a radiation side.

60. The method as in claim 58, wherein the photoelectrode is an pinpin type cell with negative voltage generated on a radiation side.

20 61. The method as in claim 59, wherein hydrogen gas is generated in the bottom compartment and exits from the first outlet tube, and wherein oxygen is generated in the top compartment and exits from the second outlet tube.

25 62. The method as in claim 60, wherein oxygen gas is generated in the bottom compartment and exits from the first outlet tube, and wherein hydrogen is generated in the top compartment and exits from the second outlet tube.

30 63. The method as in claim 61, further comprising circulating electrolyte wherein gases and electrolyte are circulated by the pumps

through first and second gas collection containers, respectively, so that hydrogen is collected at a first collection port in a first gas collection container and oxygen is collected at a second collection port in a second gas collection container; and wherein electrolyte flows from the first and second recycling ports, respectively, back into the bottom and top compartments respectively, through third and fourth inlet tubes operatively connected to a second end adaptor on and opposing end of the PEC cell.

64. The method as in claim 62, further comprising circulating electrolyte wherein gases and electrolyte are circulated by the pumps through first and second gas collection containers, respectively, so that oxygen is collected at a first collection port in a first gas collection container and hydrogen is collected at a second collection port in a second gas collection container; and wherein electrolyte flows from the first and second recycling ports, respectively, back into the bottom and top compartments respectively, through third and fourth inlet tubes operatively connected to a second end adaptor on and opposing end of the PEC cell.

65. The method as in claim 63, further comprising adding additional water via first and second water inlet valves and switches operatively connected via first and second ports, respectively, to the first and second gas collection containers to allow additional water to flow into the system.

66. The method as in claim 64, further comprising adding additional water via first and second water inlet valves and switches operatively connected via first and second ports, respectively, to the first and second gas collection containers to allow additional water to flow into the system.

67. The PEC cell of claim 1, wherein the electrode comprises: metal substrate, metal reflector, transparent conducting oxide (TCO), n-type a-Si layer, intrinsic a-SiGe layer or microcrystalline silicon layer, p-type a-Si based layer, n-type a-Si layer, intrinsic a-Si layer or a-SiGe layer, p-type a-Si based layer, n-type a-Si layer, intrinsic a-Si layer, p-type a-Si based layer (nipnipnip layers), TCO layer.

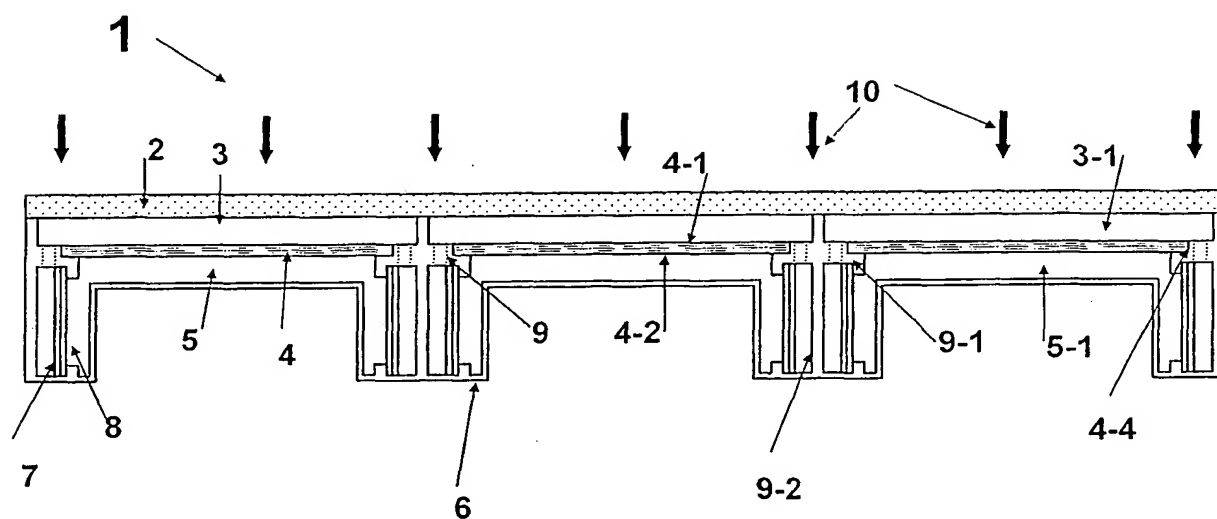
68. The PEC cell of claim 67 wherein the substrate is coated with a hydrogen evolution catalyst and the top TCO layer is covered with an oxygen evolution catalyst 11.

69. The PEC cell of claim 68 wherein top TCO layers comprise at least one of tin oxide and fluorine-doped tin oxide.

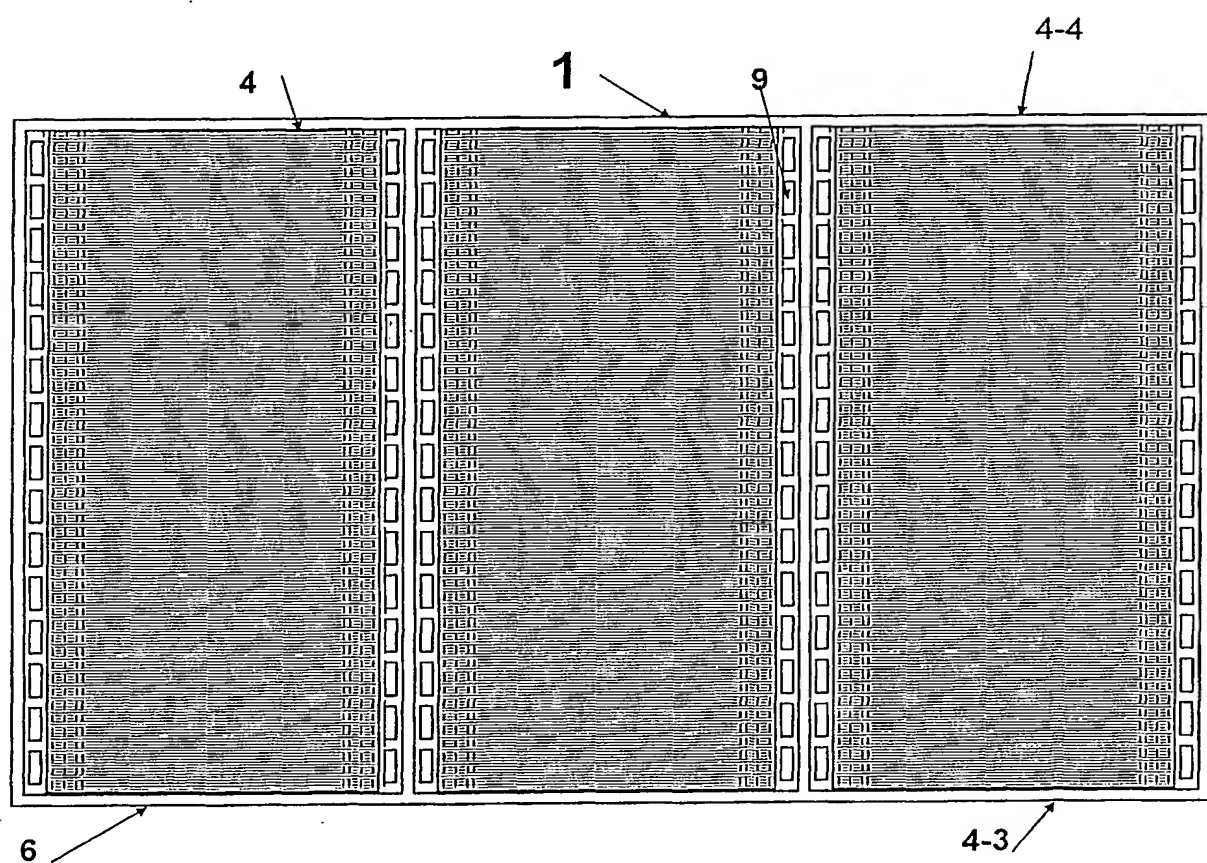
70. The PEC cell of claim 1, wherein the electrode comprises: metal substrate, metal reflector, transparent conducting oxide (TCO) layer, p-type a-Si based layer, intrinsic a-SiGe layer or microcrystalline silicon layer, n-type a-Si layer, p-type a-Si based layer, intrinsic a-Si layer or a-SiGe layer, n-type a-Si layer, p-type a-Si based layer, intrinsic a-Si layer, n-type a-Si layer (pinpinpin layers), TCO layer.

71. The PEC cell of claim 70, wherein the substrate is coated with an oxygen evolution catalyst and the top TCO layer is covered with a hydrogen evolution catalyst.

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**FIG. 1a**



**FIG. 1b**

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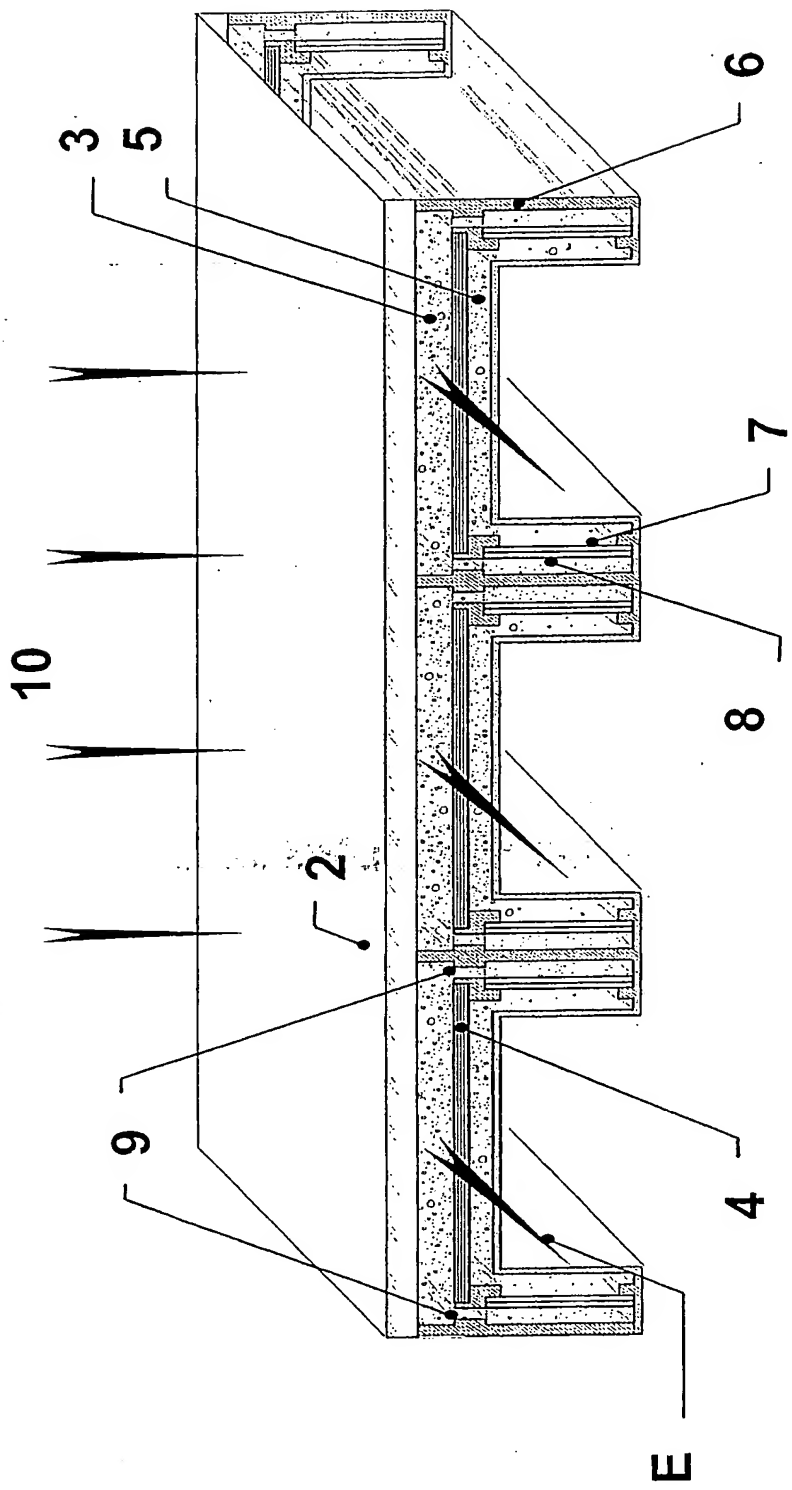


FIG. 1c

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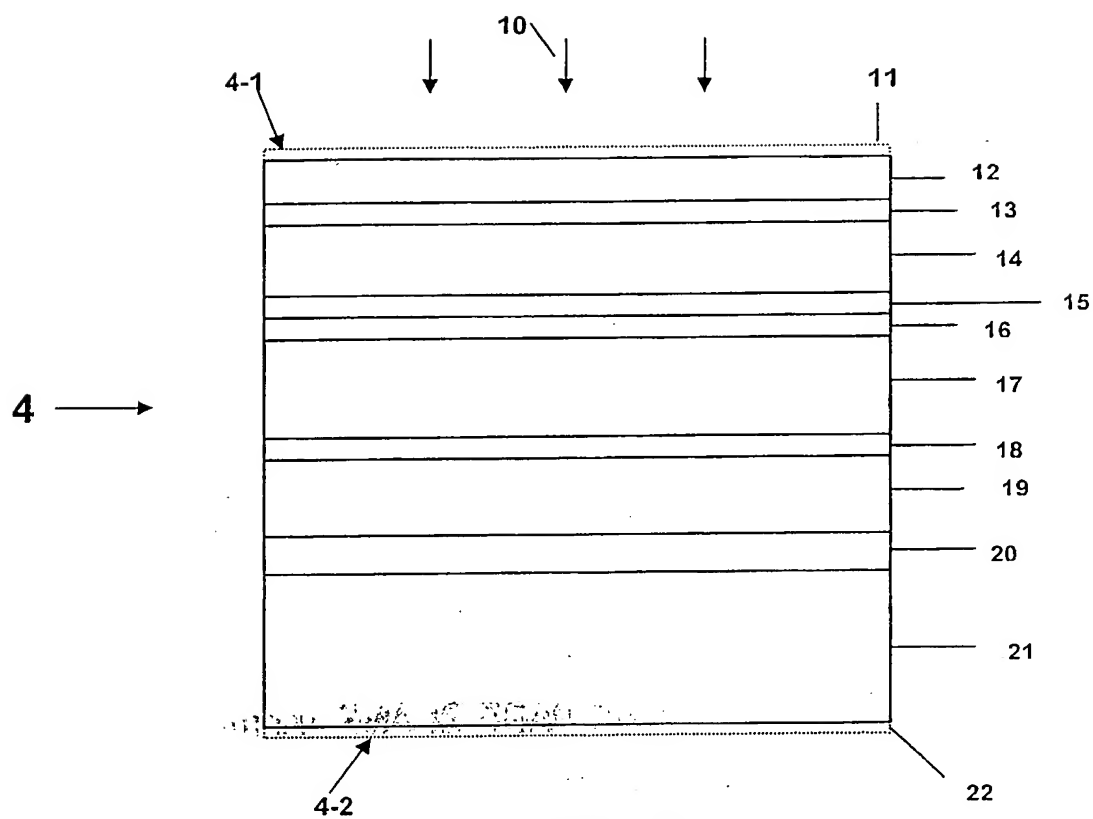


Fig. 2

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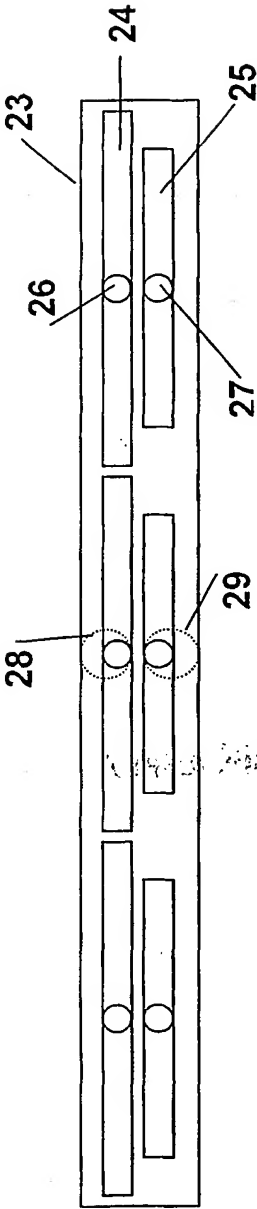


FIG. 3a

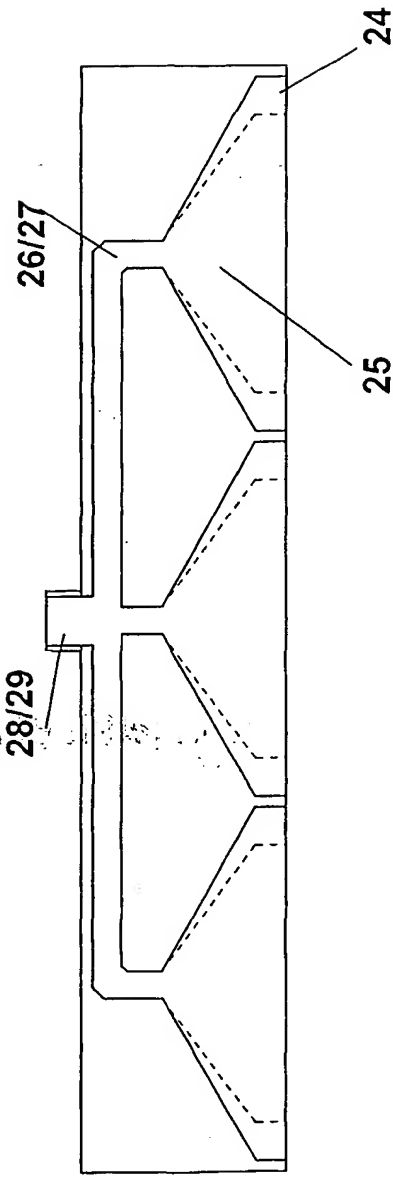


FIG. 3b

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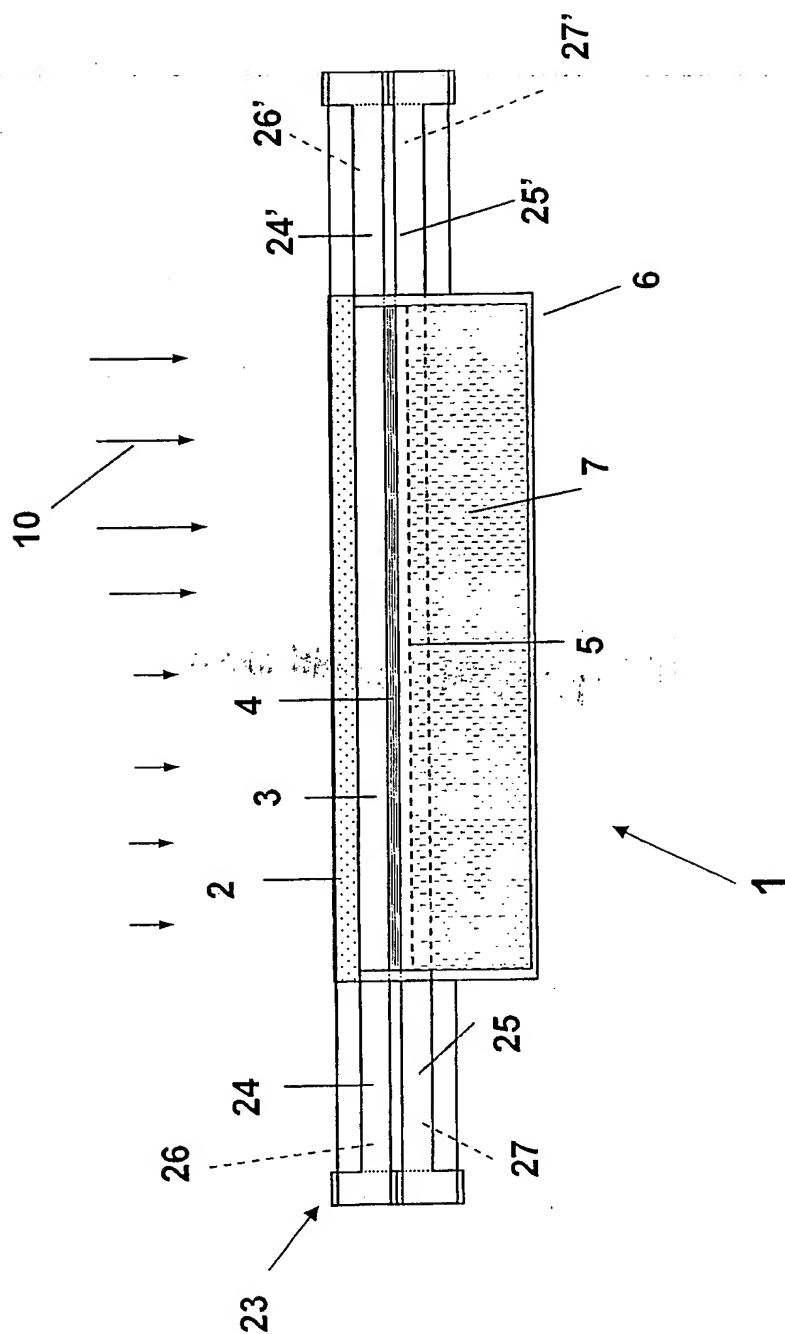
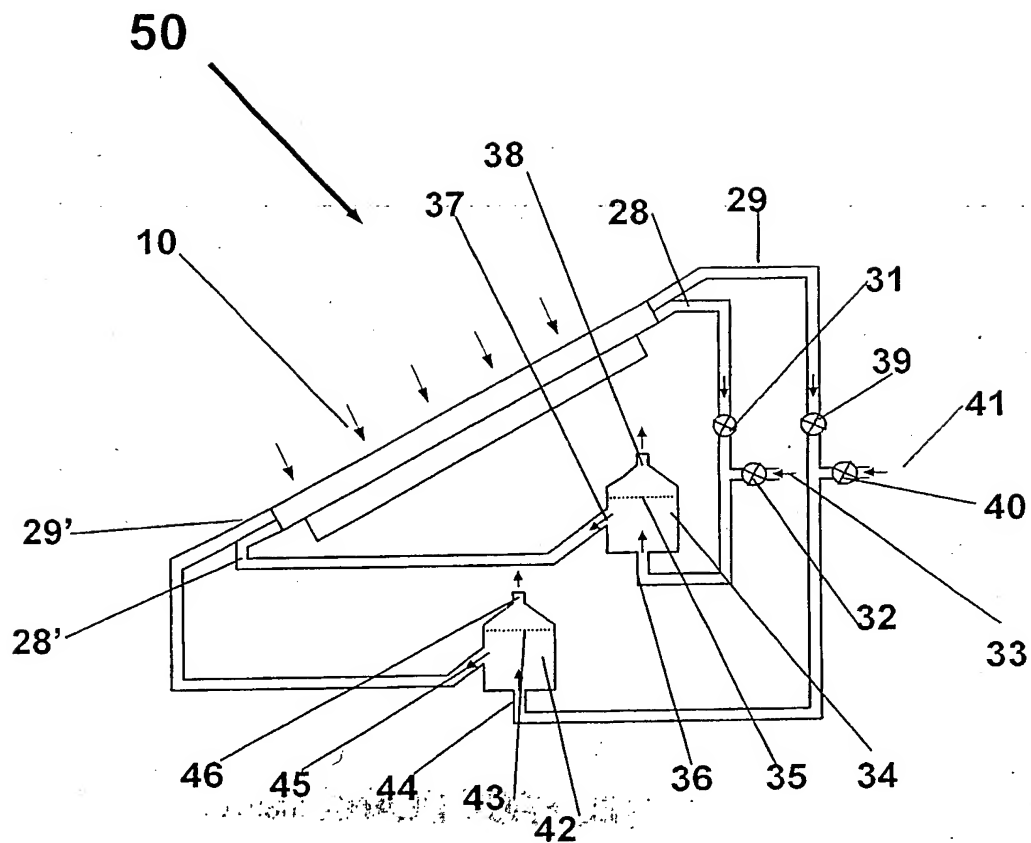


FIG. 4

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**FIG. 5**

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/37543

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C25D 17/00  
US CL : 204/242, 252

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : 204/242, 252

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST: photovoltaic, photoelectrochemical, photoelectrode, membrane

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,501,804 A (BOCKRIS et al) 26 February 1985 (26.02.1985), columns 3-5..	1-9, 12-18, 23, 25
Y	US 4,643,817 A (APPLEBY) 17 February 1987 (17.02.1987), column 3-4.	1-9
Y	US 4,511,638 A (SAPRU et al) 16 April 1985 (16.04.1985), column 5, lines 25-68; column 6, lines 1-5.	1-9, 11-13, 25-29, 35, 70
Y	US 4,315,973 A (MANASSEN et al) 16 February 1982 (16.02.1982), column 3, lines 5-50.	1
Y	US 4,427,729 A (GRAETZEL et al) 24 January 1984 (24.01.1984), column 2, lines 13-55; column 3, lines 1-16.	1-3, 25-27, 30, 34, 36, 70

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
12 March 2004 (12.03.2004)

Date of mailing of the international search report  
09 APR 2004

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